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12 a. DISTRIBUTION / AVAILABILITY STATEMENT

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13. ABSTRACT (Maximum 200 words)

The objective of this research was to develop a novel low-temperature route to the structurally controlled nanofabrication of bimetallic-oxide semiconductors, with controlled order, stoichiometry and spacing of the bimetallic centers on the atomic- and nanoscale, to deliver materials with never-before observed electronic properties resulting from the controlled electronic interactions of the two metal centers. Our approach took advantage of two recent developments: (i) a new biologically-inspired low-temperature synthesis method we recently developed, and (ii) the synthesis of defined molecular precursors of bimetallic oxides, thereby extending our synthesis method from single metal oxide materials to *bimetallic* oxide (and sulfide-oxide) ferroelectric and optoelectronic semiconductor materials, to obtain control over structure and enhancement of properties never before achievable. We report success in this project, with the resulting materials and technology transfer described offering the Army potential advantages for uncooled infrared detectors and fire- and explosion-proof lithium ion batteries.

14. SUBJECT TERMS
Semiconductors, Barium Titanate, Biotechnology, Bimetallic, Chalcogens, Chalcogenides, Materials, Electronics, Magnetic, Optoelectronic, Perovskites, Biologically Inspired, Nanofabrication, Nanostructure, Nanotechnology,

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Report Documentation Page (SF298) Continuation Sheet (Enclosure 2):

(1) List of papers submitted or published under ARO sponsorship during this reporting period.

(a) Manuscripts submitted, but not published:

Morse, D. E. 2007. Biotechnology opens new routes to high-performance materials for improved photovoltaics, batteries, uncooled IR detectors, ferroelectrics and optical applications. Proc. Army Sci. Conf. Orlando, 2007. (in press).

(b) Papers published in peer-reviewed journals:

Roth, K.M., Y. Zhou, W. Yang and D.E. Morse. 2005. Bifunctional small molecules are biomimetic catalysts for silica synthesis at neutral pH, J. Amer. Chem. Soc. 127: 325 - 330.

Kisailus, D., J.H. Choi, J. C. Weaver, W. Yang and D.E. Morse. Enzymatic synthesis and nanostructural control of gallium oxide at low temperature. 2005. Advanced Materials 17: 314-318.

Kisailus, D., M. Najarian, J. C. Weaver, and D.E. Morse. 2005. Functionalized gold nanoparticles mimic catalytic activity of a polysiloxane-synthesizing enzyme. Advanced Materials 17 [10]: 1234-1239 (cover article).

Schwenzer, B., K.M. Roth, J. R. Gomm, Meredith Murr & D. E. Morse. 2006. Kinetically controlled vapor-diffusion synthesis of novel nanostructured metal hydroxide and phosphate films using no organic reagents. J.Mater. Chem. 16: 401 - 407.

Kisailus, D., Y. Amemiya, J. C. Weaver, Q. Truong and D.E. Morse. 2006. Self-assembled bi-functional surface mimics an enzymatic and templating protein for low-temperature synthesis of a metal oxide semiconductor. Proc. Natl. Acad. Sci. USA 103: 5652-5657.

Brutchey, R.L., E. S. Yoo, and D. E. Morse. 2006. Biocatalytic synthesis of a nanostructured and crystalline bimetallic perovskite-like barium oxofluorotitanate at low temperature. J. Amer. Chem. Soc. 128: 10288-10294.

Kisailus, D. J., B. Schwenzer, J. Gomm, J. C. Weaver and D. E. Morse . 2006. Kinetically controlled nucleation of zinc oxide thin films at low temperatures. J. Amer. Chem. Soc. 128: 10276-10280.

Brutchey, R.L. and D.E. Morse. 2006. Template-free, low-temperature synthesis of crystalline barium titanate nanoparticles under bio-inspired conditions. Angewandte Chemie Intl. Ed. 45: 6564-6566.

Schwenzer, B., J.R. Gomm and D.E. Morse. 2006. Substrate-induced growth of nanostructured zinc oxide films at room temperature using concepts of biomimetic catalysis. . Langmuir 22: 9829-9831.

(c) Papers published in non-peer-reviewed journals or in conference proceedings:

None

(d) Papers presented at meetings, but not published in conference proceedings:

03/05	Invited Lecture, “New Biologically Inspired Low-Temperature Nanofabrication Methods Yields Semiconductors for Photovoltaic and Other Applications”	American Chemical Society Symposium, San Diego, CA
03/05	Invited Lecture, “New Biologically Inspired Low-Temperature Nanofabrication Yields Semiconductors for Photovoltaic and Other Applications”	Center for Biologically Inspired Materials and Material Systems, Duke University, Durham, NC
04/05	Invited Lecture, “New Biologically Inspired Low-Temperature Synthesis Yields Metal Oxide Semiconductors for Photovoltaic and Other Applications”	MRL Workshop, University of Kyoto, Kyoto, Japan
04/05	Invited Lecture, “Low-Temperature Routes to Semiconductors and Metal Oxides for Energy and Electronic Applications”	ICB Army-Industry Conference, University of California, Santa Barbara, Santa Barbara, CA
04/05	Invited Lecture, “New Biologically Inspired Low-temperature Synthesis of Metal Oxide Semiconductors, Silica and Silsesquioxanes for Photovoltaic and Other Applications”	Biotechnology Industry and Army Forum, UCSB
05/05	Invited presentation, “Biological Inspiration and Biomimetic Routes to Advanced materials	Institute for Biologically Inspired Materials, University of North Carolina, Durham, NC
06/05	Invited Seventh Kelly Lecture, “Biologically Inspired Routes for Materials Synthesis and Nanofabrication: High Performance with Low Environmental Impact”	Cambridge University Armourers and Braisers’ Forum, Cambridge, England
06/05	Contributed Presentation, “New Biologically Inspired Low-temperature Nanofabrication of Metal Oxide Semiconductors for Photovoltaic and Other Applications”	International TMS Symposium on Electronic Materials, Santa Barbara, CA
07/05	Invited Lecture, “Translating Biological Mechanisms into Practical Routes for Nanofabrication”	International Symposium on Advances in Network Sciences, Nano-, Bio- and Information Technology, Singapore
08/05	Invited Presentation ”Biologically Inspired Routes to Novel Materials with Advantages for Photovoltaics, Lithium-ion Batteries and Other Energy Applications”	Biomolecular Materials for Energy Applications Conference, , Warrentown, VA
08/05	Invited Lecture, "New Biologically Inspired Low-Temperature Synthesis of Semiconductors for Photovoltaic and Other Applications”	International Center for Materials Research Summer Program on Biomaterials; ICMR, MRL, UCSB
10/05	Invited Lecture, "Biologically Inspired Self-Healing Materials: From Proteins in Bone and Shell to Novel Synthetic Materials"	NASA Langley Aerospace Research Center; Hampton, VA
10/05	Keynote Lecture, “Bio-Nanotechnology and the Reality of Prospects for Revolutionary New Materials for Medical Applications”	11^{th} Annual Cancer Research Symposium, UC Davis-NIH Cancer Research Center, Sacramento, CA
11/05	Keynote Lecture, "Biotechnology Reveals Novel Routes to Low-temperature Nanofabrication of Semiconductors for Photovoltaics and Advanced Optoelectronics"	3rd International Symposium on Biology and Nanotechnology, Miyazaki, Japan.
12/05	Invited Lecture, “Structure-Directing Enzyme from Sponge Biosilica and Its Biomimetics Catalyzes and Templates synthesis of Silica, Silsesquioxanes and Metal Oxides at Low Temperature and Neutral pH”	International Pacifichem Symposium on Aqueous Chemistry and Biochemistry of Silicon, Honolulu, HI
01/06	Keynote Lecture, "Biomolecular Mechanism of Silica Synthesis Opens Novel Routes to Nanofabrication of Semiconductors and Other Advanced Materials”	2^{nd} ASM-IEEE-EMBS International Symposium on Bio, Micro and Nanosystems, San Francisco, CA

01/06	Invited Lecture, “Opportunities for Research at the Convergence of Biotechnology and Engineering: Biomolecular Mechanism of Silica Synthesis Opens Novel Routes to Low-Temperature Nanofabrication of Semiconductors and Other Advanced Materials”	University of Delaware, Delaware Biotechnology Institute, Newark, DE
02/06	Keynote Lecture, “Research at the Interface Between Biotechnology, Nanotechnology and Engineering”	Symposium on Science and Technology (“Timing Change in Changing Times”), Association of the U.S. Army, Ft. Lauderdale, FL
02/06	Invited Lecture, “Molecular Mechanisms of Biomineralization in Abalone Shell and Pearl: New Routes to Synthesis of High-Performance Composite Materials"	Sixth International Abalone Symposium, Puerto Varas, Chile
03/06	Invited Lecture, “Biomolecular Mechanism of Silica Synthesis Opens Novel Routes to Low-Temperature Nanofabrication of Silicones, Semiconductors, Ferroelectrics and Other Advanced Materials”	General Electric Corp. Global Research Center, Niskayuna, NY
03/06	Invited Lecture, “Bio-Inspired, Kinetically Controlled Low-Temperature Catalytic Nanofabrication of Template-Free Metal Hydroxide, Phosphate and Oxide thin Films”	American Chemical Society Symposium, Atlanta, GA
03/06	Invited Seminar, “Molecular Mechanisms of Biomineralization in Molluscan Shell and Pearl: New Routes to Synthesis of High-Performance Composite Materials”	Materials Department and Department of Biochemistry, Johns Hopkins University, Baltimore Washington
04/06	Invited Lecture, “Biomolecular Mechanism of Silica Synthesis Opens Novel Routes to Low-Temperature Nanofabrication of Silicones, Semiconductors, Ferroelectrics and Other Advanced Materials”	California NanoSystems Institute, University of California, Los Angeles, CA
04/06	Keynote Lecture, "Biomolecular Mechanisms Governing Materials Nanofabrication - Applications to Medical Diagnostics and Therapeutics"	Nanotechnology and Life Sciences Symposium, Burnham Institute, San Diego, CA
05/06	Invited Lecture, " Biologically Inspired Nanofabrication”	Second International Conference on Synthetic Biology; University of California, Berkeley, CA
5/06	Televised Research Colloquium Presentation, "Bio-inspired Low-Temperature Nanofabrication of Silica and Polymer Microcapsules for Targeted Delivery of Labile Protein Therapeutic Agents"	Televised research colloquium presentation to UCSD and UCSB participants in NIH-sponsored Center for Nanotechnology-Based Improvements in Cancer Diagnosis and Treatment
08/06	Invited Lecture, “Biomolecular Mechanism of Silica Synthesis Opens Novel Routes to Low-Temperature Nanofabrication of Silicones, Semiconductors, Ferroelectrics and Other Advanced Materials”	BASF International Symposium on Bio-Inspired Synthesis for the Chemical Industry, Strasbourg, France
08/06	Invited Lecture, “Biomolecular Mechanism of Silica Synthesis Opens Novel Routes to Low-Temperature Nanofabrication of Silicones, Semiconductor, Ferroelectrics and Other Advanced Materials”	Symposium on Evolution of Nature-Guided Materials Processing, Nagoya University, Japan
09/06)	Invited Presentation “KLH- and Smart Nanoparticle-Based Strategies for Tumor Targeting”	Cancer Research Conference, UC Davis-NIH Cancer Research Center, Sacramento, CA
10/06	Invited Lecture, "Dynamic Bio-Photonics: Phosphorylation of Reflectin Proteins Drives Adaptive Reflectance in Squid."	U S Army Research, Development and Engineering Command, Ft. Belvoir, VA
10/06	Invited Seminar “ Biomolecular Mechanism of Silica Synthesis Reveals Novel Protein Mechanisms and Opens New Routes to Low-Temperature Nanofabrication of Semiconductors”	Biomolecular Science and Engineering Program Seminar Series, UCSB

(2) Demographic Data for this Reporting Period:

(a) Number of Manuscripts submitted during this reporting period:	10
(b) Number of Peer Reviewed Papers submitted during this reporting period:	9
(c) Number of Non-Peer Reviewed Papers submitted during this reporting period:	None
(d) Number of Presented but not Published Papers submitted during this period	31

(3) Demographic Data for the life of this agreement:

(a) Number of Scientists Supported by this agreement (decimals are allowed)	5
(b) Number of Inventions resulting from this agreement	1
(c) Number of PhD(s) awarded as a result of this agreement	1
(d) Number of Bachelor Degrees awarded as a result of this agreement	4
(e) Number of Patents Submitted as a result of this agreement	1
(f) Number of Patents Awarded as a result of this agreement	1
(g) Number of Grad Students supported by this agreement	2
(h) Number of FTE Grad Students supported by this agreement	2
(i) Number of Post Doctorates supported by this agreement	1
(j) Number of FTE Post Doctorates supported by this agreement	1
(k) Number of Faculty supported by this agreement	1
(l) Number of Other Staff supported by this agreement	0
(m) Number of Undergrads supported by this agreement	4
(n) Number of Master Degrees awarded as a result of this agreement	1

(3) "Report of inventions" (by title only)

Biologically Inspired Synthesis of Thin-Film Materials (provisional patent filed)

(4) "Scientific progress and accomplishments" (Description should include significant theoretical or experimental advances) and

Background and Need for this Research: The Army, other branched of the DoD and other sectors all require development of increasingly high-performance electronic, optoelectronic and magnetic materials for improved data acquisition, analysis, storage, communications and control. The conventional preparative techniques for many metal oxide or metal chalcogenide materials, however, are via solid-state reactions at high temperatures (> 1000 ˚C) – manufacturing conditions that increasingly are proving incompatible with integration with many delicate components now needed for these applications. There is thus increased interest in the development of novel biologically inspired and "chimie douce" (soft chemistry) routes to electronic materials that employ solution phase syntheses at low to moderate temperatures (e.g., Morse, 1999, *Trends in Biotechnology* 17: 230-232; Figlarz, 1994, *Mater. Sci. Forum* 55: *152-153*).

Highest impact results: We have developed a unique biologically inspired low-temperature route to the synthesis of barium titanate and other bimetallic oxide perovskite materials with advantages over previously used high-temperature synthesis methods. The materials produced by the method developed in this research exhibit a high degree of crystallinity, low polydispersity (in the size range of ca. 6 nm) and a lack of phase-segregation that typically results from conventional high temperature synthesis methods and compromises behavior of the resultant material.

These findings are reported in detail in: Brutchey, R.L., E. S. Yoo, and D. E. Morse. 2006. Biocatalytic synthesis of a nanostructured and crystalline bimetallic perovskite-like barium oxofluorotitanate at low temperature. *J. Amer. Chem. Soc.* 128: 10288-10294; and Brutchey, R.L. and D.E. Morse. 2006. Template-free, low-temperature synthesis of crystalline barium titanate nanoparticles under bio-inspired conditions. *Angewandte Chemie Intl. Ed.* 45: 6564-6566.

We currently are collaborating with the Army Research Laboratory and The Aerospace Corporation (El Segundo, CA) in an effort to use the barium titanate nanoparticles made by this new synthesis procedure for an improvement in resolution of uncooled infrared detectors. We are collaborating with the Army's CERDEC and Quallion, Inc. (Sylmar, CA) to take advantage of the strong Positive Thermal Coefficient of Resistance (PTCR) provided by the barium titanate nanoparticles made by this procedure to provide a self-quenching coating on battery electrodes, thereby making Li-ion batteries fire- and explosion-proof. We also are collaborating with IBM, one of the world's leading producers of information-storage materials and systems, to explore the potential application of the synthesis method we developed to improve the manufacturing of bimetallic oxides for magnetic information storage.

Our approach: The objective of this research was to develop a novel low-temperature route to the structurally controlled nanofabrication of bimetallic-oxide semiconductors, with controlled order, stoichiometry and spacing of the bimetallic centers on the atomic- and nanoscale, to deliver materials with never-before observed electronic properties resulting from the controlled electronic interactions of the two metal centers. Our approach took advantage of two recent developments: (i) a new biologically-inspired low-temperature synthesis method we recently developed, and (ii) the synthesis of defined molecular precursors of bimetallic oxides, thereby extending our synthesis method from single metal oxide materials to *bimetallic* oxide (and sulfide-oxide) ferroelectric and optoelectronic semiconductor materials, to obtain control over structure and enhancement of properties never before achievable. We are pleased to report success in this project, with the resulting materials and technology transfer described offering the Army potential advantages for uncooled infrared detectors and fire- and explosion-proof lithium ion batteries.

We employed a bilateral approach to the synthesis of crystalline mixed metal perovskite ceramics and metal chalcogenide materials. First, we used the mechanisms we discovered that underlie the biological synthesis of nanostructured silica, and that we found can be harnessed for the low-temperature nanofabrication of a wide range of semiconductors. We previously demonstrated that the structure-directing enzyme silicatein can catalyze the hydrolysis and polycondensation of precursors of silica and metal oxide semiconductors (e.g., TiO_2 and Ga_2O_3) while simultaneously templating the nanoscale structure of the resulting material (e.g., Sumerel et al., 2003, *Chem. Mater.* 15: 4804-4809; Kisailus et al., 2005. *Advanced Materials* 17: 314-318). A particularly useful aspect of this approach is the inherently benign conditions that it utilizes (e.g., neutral pH, ambient temperature and pressure, and the absence of caustic chemicals), matching the conditions now desired by the electronics industry.

The second aspect of our approach was motivated by the fact that is difficult to form single-phase crystalline materials under ambient conditions when more than one metal is present (e.g., to form bimetallic oxides such as $BaTiO_3$ or metal chalcogenides such as M_xS_y) because of the strong potential for phase segregation of the two metals, metal oxides or metal sulfides. For this reason, we designed and synthesized unique molecular precursors that contain multiple heteroelements in one discreet molecular complex (cf. Figure 1). The establishment of M^1–O–M^2 or M–S(Se) linkages with fixed stoichiometry and atomic geometry in the molecular precursor has been shown even under high-temperature synthesis conditions to produce a higher

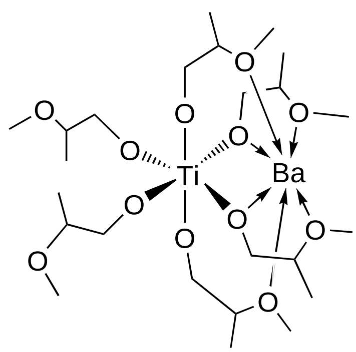

Figure 1. Idealized structure of a barium titanium mixed alkoxide.

abundance of M^1–O–M^2 or M–S(Se) linkages upon conversion to the bulk material (Fujdala and Tilley,2003, *J. Catal. 216*: 265. We have now confirmed our expectatation that using such predesigned bimetallic precursors in conjunction with our low-temperature biologically inspired structure-directing catalysts thus leads to even better homogeneity, and that the distinct spatial arrangement of elements in the molecular precursors might lead to unique optical, electronic, and magnetic properties upon conversion to a material. We have proved that this approach offers molecular control over bulk properties of the target materials.

New routes to ferroelectric perovskites. Low temperature solution routes to perovskite ceramics, such as $BaTiO_3$, had previously produced only amorphous materials; either a hydrothermal step under strongly alkaline conditions or a high-temperature annealing step (> 600 ˚C) is typically required to form crystalline $BaTiO_3$ (Lee et al., 1997, *Langmuir 13*: 3866). Using the methods outlined above, we have successfully demonstrated that by carefully controlling the amount of water added to an alcoholic solution of a barium titanium mixed alkoxide molecular precursor, nanocrystalline $BaTiO_3$ can be synthesized under mild conditions (neutral pH and ≤ 50 ˚C; see eq. 1). The crystallinity of the resulting $BaTiO_3$ was confirmed by powder X-ray diffraction, selected area electron diffraction, and Raman spectroscopy. We demonstrated that this method is highly generic, proving useful with a variety of mixed metal alkoxide molecular precursors and a number of biological and biomimetic hydrolysis/condensation catalysts, yielding significantly improved nanostructural control of the resulting material.

$$\text{Ba/Ti mixed alkoxide} \quad + \quad n\ H_2O \xrightarrow[\text{Š 50 ÞC}]{\text{alcohol}} \begin{matrix}\text{nanocrystalline}\\ BaTiO_3\end{matrix} \qquad (1)$$

New routes to metal chalcogenides. Metal chalcogenide materials are typically made via solid-state syntheses or by MOCVD routes that require high temperature, low pressures, and other restrictive conditions. The ability to synthesize metal chalcogenides via soft chemical routes is an attractive goal; however, this has been complicated by the chemistry involved in the hydrolysis/condensation mechanism of sol-gel processes (i.e., toxic, gaseous H_2S would be required as a hydrolysis reagent rather than H_2O).

A previously reported solution-phase route to metal chalcogenides not requiring H_2S utilizes a number of anionic metal sulfide clusters have been used as precursors for M_xS_y materials under acidic aqueous conditions. For example, the molecular precursor $[Me_4N]_4Ge_4S_{10}$ (Figure 2) has been successfully used as a molecular precursor to crystalline GeS_2 (MacLachlan, et al., 1998, *Angew. Chem. Int. Ed. 37*: 2075). Under very acidic conditions, the basic thiolate groups on the precursor protonate and then condense to form a Ge–S–Ge network material built up from the adamantane-like subunits.

We also explored biocatalytic routes to GeS_2 using $[Me_4N]_4Ge_4S_{10}$ with the small molecule biomimetic catalysts we recently developed (Roth et al., 2005, *JACS* 127:325). These catalysts permit synthesis at neutral pH, thus allowing us to avoid the acidic conditions previously used by others. We have observed that the materials prepared via these biocatalytic routes possess unique particle morphologies and potentially useful optical properties when compared to the GeS_2 prepared with hydrochloric acid. The origin of these unique properties is currently under investigation.

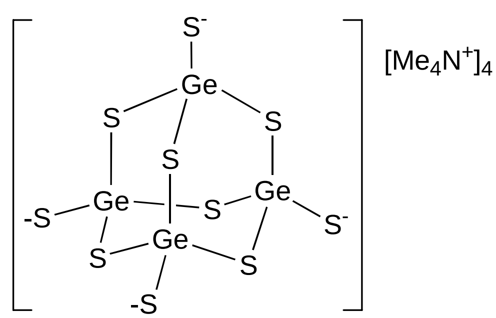

Figure 2. $[Me_4N]_4Ge_4S_{10}$ molecular precursor with adamantane-like structure.

(5) "Technology transfer"

We currently are collaborating with the Army Research Laboratory and The Aerospace Corporation (El Segundo, CA) in an effort to use the barium titanate nanoparticles made by this new synthesis procedure for an improvement in resolution of uncooled infrared detectors. We are collaborating with the Army's CERDEC and Quallion, Inc. (Sylmar, CA) to take advantage of the strong Positive Thermal Coefficient of Resistance (PTCR) provided by the barium titanate nanoparticles made by this procedure to provide a self-quenching coating on battery electrodes, thereby making Li-ion batteries fire- and explosion-proof. We are collaborating with IBM, one of the world's leading producers of information-storage materials and systems, to explore the potential application of the synthesis method we developed to improve the manufacturing of bimetallic oxides for magnetic information storage.